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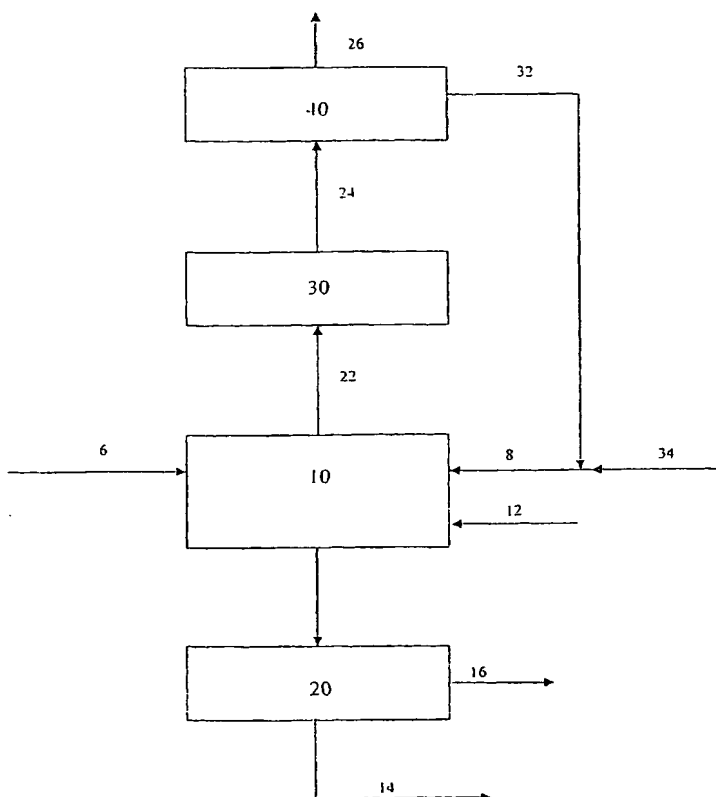
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(54) Title: METHOD OF LEACHING BERYLLIUM FROM BERYLLIUM-CONTAINING ORES USING FLUOSILICIC ACID



(57) Abstract: A production process for dissolving beryllium in a beryllium feed source by means of fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ), including the steps of: (a) providing the beryllium feed source, and (b) reacting the beryllium feed source with a source of fluosilicic acid in a reaction stage to produce dissolved beryllium in an aqueous solution.

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## METHOD OF LEACHING BERYLLIUM FROM BERYLLIUM-CONTAINING ORES USING FLUOSILICIC ACID

### FIELD OF THE INVENTION

5       The present invention relates to a method of leaching beryllium values from beryllium-containing ores, such as beryl, bertrandite, and/or phenakite, and more particularly, to a method of leaching beryllium values from beryllium-containing ores using fluosilicic acid.

### 10   BACKGROUND OF THE INVENTION

Beryllium (Be) is one of the lightest of all metals and has one of the highest melting points of any light metal. Beryllium metal and its alloys are used principally in aerospace and defense applications because of its stiffness, low specific gravity, and dimensional stability over a wide temperature range. Beryllium metal is stiffer than  
15 1010 steel, and is also highly conductive. Beryllium and alloys thereof are often the preferred materials for electronic equipment. Beryllium-copper alloys are used in a variety of applications because of their electrical and thermal conductivity, high strength and hardness, good corrosion resistance and fatigue resistance, and non-magnetic properties. Beryllium oxide is an excellent heat conductor, with high strength  
20 and hardness, and acts as an electrical insulator in some applications.

Commercially, beryllium is extracted from mineral ores, primarily from beryl, bertrandite and phenakite. The composition of beryl is  $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ . Commercial Beryl contains about 12% BeO, which is close to the theoretical composition of beryl (14% BeO). The composition of bertrandite is  $4\text{BeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  
25 which, according to the theoretical chemical composition, contains 42% BeO. Commercially-available bertrandite contains only about 0.6%-0.9% BeO. Whereas the commercially-available beryl is almost a pure mineral, the commercially-available bertrandite contains only 1.0-1.5% of the pure bertrandite, admixed with additional minerals such as aluminum and iron oxides, calcium and alkali oxides or silicates and  
30 quartz.

The domestic (U.S.A.) producer price for beryllium contained in beryllium-copper master alloy was \$160 per pound in 1998, a price level that was relatively steady since 1990. Prices for other forms of beryllium have also been stable for nearly a decade. Beryllium and beryllium alloys are very often the most expensive materials available for a given application. Hence, the use of metal beryllium and compounds thereof is often precluded in all but the most exotic applications.

One major factor behind the cost of beryllium products is high production costs. Ullmann's Encyclopedia of Industrial Chemistry (Vol. 4a, Wiley-VCH Verlag GmbH & Co., pp. 15-26 (1985), which is incorporated by reference for all purposes, as if fully set forth herein, surveys the known methods for treating and dissolving beryllium ores, and for processing them into various desired beryllium compounds.

In the production of beryllium from bertrandite, boiling sulfuric acid is used to dissolve the bertrandite, along with various oxide impurities (e.g., aluminum, iron) typically present in the commercial ore. The solution is filtered to remove any insoluble silica from the solution.

One important drawback of bertrandite as a feed material is that commercially-available bertrandite contains less than 1% BeO, i.e., only 5-8% of the BeO content of commercially-available beryl.

However, the processing and dissolution of the beryllium-rich beryl is considerably more complicated, expensive, and involves additional, weighty, health and safety issues. Ullmann's Encyclopedia reports that beryl is only slightly soluble in sulfuric acid even under such extreme conditions as heating for several hours in an autoclave at 400°C, hence the beryl must be subjected to either an alkali or a heat treatment.

In the alkali treatment, finely ground beryl is heated until fusion or sintered below the melting point with a sufficient quantity of alkaline flux. Suitable alkali compounds include hydroxides or carbonates of sodium, potassium and calcium; mixtures of these carbonates; calcium oxide; borax; lead chloride; and sodium sulfate and charcoal. The ratio of flux to beryl depends on the operating conditions, especially the temperature: the higher the temperature the less flux. For alkali treatments involving molten

material, gas-heated or oil-heated rotary furnaces or blast furnaces are suitable. Rotary kilns, muffle furnaces, or tunnel kilns are used for sintering.

In the heat treatment, the beryl is melted, without additives, at a temperature exceeding 1650°C, and then quenched in water. After this treatment, about 50-60% of the beryl has an enhanced solubility in sulfuric acid. The rest of the beryllium oxide forms a solid solution with silicon dioxide that is not attacked by sulfuric acid. At 900°C, this solid solution separates into beryllium oxide and silicon dioxide components, hence, a second heat treatment at this high temperature produces a free beryllium oxide that is soluble in sulfuric acid.

After cooling and grinding to 200 mesh, the obtained powder is heated to 250°C to 300°C in concentrated sulfuric acid, reacting so as to convert the beryllium, aluminum, and any iron, to soluble sulfates. The silica fraction largely remains in the dehydrated, water insoluble form. This two-stage heat treatment renders soluble a total of about 90% of the beryllium content of the beryl.

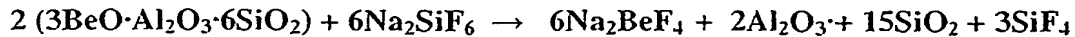
The heat-treated beryl is extracted with hot concentrated sulfuric acid, whereas alkali-treated beryl is extracted with cold sulfuric acid. While in the alkali process, there are relatively low heating costs, the total consumption of acid is considerably greater because of the alkali added.

After dilution of the liquor with water, the insoluble silicon dioxide is separated by filtration. At this point in the process, the filtrate contains not only beryllium and aluminum sulfate but also considerable quantities of iron sulfate and smaller amounts of other impurities, most of which must be removed before the precipitation of beryllium hydroxide. Many separation processes are known, including alum separation, ammonium carbonate separation, and chelate separation.

It is manifest from the above that numerous time-consuming and expensive steps are required to dissolve the beryl ore so as to obtain dissolved beryllium. Moreover, many additional steps are subsequently required to obtain high purity beryllium products from the impure beryllium solution.

Although other processes for the decomposition of beryl are known, such as the fluoride process, these have generally proven to be even more complicated and expensive than the sulfuric acid process. In the conventional fluoride process, beryl is

melted or sintered with sodium hexafluorosilicate at approximately 700°C, according to the stoichiometry of the following equation:



Aluminum oxide, silicon dioxide, and other impurities remain largely intact.

- 5 Ullmann's Encyclopedia further discloses (based on Derwin, et al., Beryllium, Butterworths, London, 1960) that the subsequent leaching step is extremely delicate:

10 The reaction product must be leached with water at room temperature because silicon dioxide is attacked by fluoride solutions at elevated temperatures. On the other hand, the leaching must be performed as rapidly as possible because otherwise the beryllium salt that is already dissolved will precipitate and in this form it is sparingly soluble, unlike the form which is present in the original fusion product.

- 15 In addition, the melting process at elevated temperatures (~700°C) is a clear disadvantage, although the sulfate process described hereinabove requires even higher temperatures.

20 Other suitable extracting agents mentioned by Ullmann's Encyclopedia (Vol. A4, p.18) are hydrogen fluoride gas at 630°C, molten fluorides, other fluorosilicates, or silicon tetrafluoride. Rotary kilns are used for reaction with the gases (hydrogen fluoride, silicon tetrafluoride); the solid mixtures (molten fluorides, other fluorosilicates) are briquetted and sintered in muffle furnaces or tunnel kilns. All of these processes are gas-phase or molten-phase processes conducted at extremely high temperatures and requiring expensive equipment.

- 25 U.S. Patent No. 3,375,060 to Olson, et al. discloses a method of solubilizing beryllium values in a mineral by reacting the mineral with fluorite ( $\text{CaF}_2$ ) and sulfuric acid. The reaction takes place at a temperature of 200°C - 300°C and atmospheric pressure. The products of the reaction are gaseous hydrogen fluoride and a salt cake containing water soluble beryllium sulfate along with calcium sulfate, aluminum sulfate, iron sulfate and various impurities. Separation of beryllium values from the solid calcium sulfate is subsequently performed by leaching with water.
- 30

At atmospheric pressure, operation at elevated temperatures of 200°C - 300°C is possible only due to the boiling-point elevation provided by a great excess of concentrated sulfuric acid. Indeed, U.S. Patent No. 3,375,060 stipulates that the concentration of the sulfuric acid feed material must be at least 60% by weight, and preferably at least 96% by weight. Moreover, the feed ratio of sulfuric acid to solid feed (i.e., the weight of H<sub>2</sub>SO<sub>4</sub> per unit weight of fluorite and beryllium-containing mineral) must be at least 1 to 1, and preferably about 1.4 to 1.

Various disadvantages are manifest in this process, including high temperature and severe reaction conditions, downstream processing of the excess sulfuric acid, ecological issues pertaining to the impurity-containing CaSO<sub>4</sub> by-product cake, the calcination process at 500°C - 600°C to render iron and aluminum less soluble, and the concentration of the very dilute beryllium-containing solution. In addition, the hydrogen fluoride co-product limits the applicability of the process.

U.S. Patent No. 3,375,060 to Zimmermann teaches a method of decomposing beryl and beryl-containing minerals by reacting powdered beryl with gaseous hydrogen fluoride at 100°C - 900°C. Preferably, the reaction is performed at 500°C - 600°C.

The products of the reaction are SiF<sub>4</sub> vapor (which is condensed with water to produce SiO<sub>2</sub>) and a cake containing water-soluble beryllium fluoride along with aluminum fluoride, iron fluoride and various impurities. Separation of beryllium values from the cake is subsequently performed by leaching with hot water.

The main disadvantages in the above-described process relate to the use of hydrogen fluoride in the vapor phase. Operation at elevated temperatures of 100°C - 900°C, and preferably, at 500°C - 600°C, requires extremely high pressures, tremendous superheating, or both. In the case of superheating, an extremely large reaction volume is required. Operation at elevated pressures requires special equipment. In particular, operation above about 200°C requires exotic materials of construction that render the process impractical.

Moreover, these extreme operating conditions raise various safety and ecology issues related to the processing of beryllium compounds. Although solid beryllium poses no health hazard, inhaling beryllium particles or fumes can trigger acute or chronic lung disease. Chronic beryllium disease, or berylliosis, is an allergic reaction to

beryllium resulting in inflammation and scarring of the lungs and inhibiting oxygenation of the bloodstream. Symptoms include shortness of breath, dry cough, chest pain, fatigue, weight loss and loss of appetite. Exposure to beryllium for an eight-hour work period should not exceed 2 micrograms of beryllium/m<sup>3</sup>. A brief exposure  
5 should not exceed 25 micrograms/m<sup>3</sup>.

There is therefore a recognized need for, and it would be highly advantageous to have, a simple and economical process for producing dissolved beryllium that overcomes the numerous and manifest deficiencies of the processes known in the art. It would be of further advantage to have a process that is safer and more ecologically  
10 friendly with respect to these known processes.

### SUMMARY OF THE INVENTION

The present invention is a method of treating a beryllium feed material, such as a beryllium-containing ore, by reacting the beryllium feed material with fluosilicic acid.

15 According to the teachings of the present invention there is provided a production process for dissolving beryllium in a beryllium feed source by means of fluosilicic acid (H<sub>2</sub>SiF<sub>6</sub>), the process including the steps of: (a) providing the beryllium feed source, and (b) reacting the beryllium feed source with the fluosilicic acid in a reaction stage to produce dissolved beryllium in an aqueous solution.

20 According to further features in the described preferred embodiments, the beryllium feed source contains a source of silica, and the method further includes the step of: (c) subjecting the source of silica and the fluosilicic acid to a reaction, so as to produce silicon tetrafluoride and water.

25 According to still further features in the described preferred embodiments, the process further includes the step of: (d) selectively evaporating the silicon tetrafluoride with respect to the dissolved beryllium.

According to still further features in the described preferred embodiments, the reaction stage contains a solid residue along with the aqueous solution, and the method further includes the step of: (c) separating the aqueous solution from the solid residue.

30 According to still further features in the described preferred embodiments, the reacting is performed at a temperature above 60°C.



According to still further features in the described preferred embodiments, the aqueous solution includes beryllium fluosilicate.

According to still further features in the described preferred embodiments, the aqueous solution includes beryllium fluoride.

5        According to still further features in the described preferred embodiments, the aqueous medium contains the fluosilicic acid and at least a second acid, the second acid having a concentration of less than 10% by weight.

According to still further features in the described preferred embodiments, the second acid has a concentration of less than 5% by weight.

10       According to still further features in the described preferred embodiments, the second acid has a concentration of less than 2% by weight.

According to still further features in the described preferred embodiments, the second acid is selected from the group consisting of hydrochloric acid, hydrofluoric acid, and phosphoric acid.

15       According to still further features in the described preferred embodiments, the second acid is sulfuric acid.

According to still further features in the described preferred embodiments, the beryllium feed source includes beryl.

20       According to still further features in the described preferred embodiments, the beryllium feed source is directly introduced to the reaction stage.

According to still further features in the described preferred embodiments, the reacting is performed at a pressure exceeding atmospheric pressure.

25       According to still further features in the described preferred embodiments, the process further includes the step of: (e) reacting the silicon tetrafluoride with water to produce silica and regenerated fluosilicic acid.

According to still further features in the described preferred embodiments, the process further includes the step of: (f) recycling at least a portion of the regenerated fluosilicic acid to the reaction stage.

30       According to still further features in the described preferred embodiments, the reacting of the silicon tetrafluoride with the water includes cooling to a temperature below 75°C.

According to still further features in the described preferred embodiments, an excess of the fluosilicic acid is introduced to the process, such that at least a portion of the regenerated fluosilicic acid is removed as a co-product.

5 According to still further features in the described preferred embodiments, the beryllium feed source includes a beryllium-containing material selected from the group consisting of bertrandite and phenakite, and the aqueous medium contains less than 10 weight % of sulfuric acid.

According to still further features in the described preferred embodiments, the aqueous medium contains less than 5 weight % of sulfuric acid.

10 According to still further features in the described preferred embodiments, the reacting is performed at a temperature below 200°C.

According to still further features in the described preferred embodiments, the reacting is performed at a temperature below 150°C.

15 According to still further features in the described preferred embodiments, the evaporation of the silicon tetrafluoride is controlled so as to selectively precipitate, with respect to the dissolved beryllium, at least one impurity from solution.

According to still further features in the described preferred embodiments, the at least one impurity is a fluoride.

20 According to still further features in the described preferred embodiments, the at least one impurity includes a cation selected from the group consisting of aluminum and iron cations.

According to still further features in the described preferred embodiments, the pH of the aqueous solution is controlled so as to selectively precipitate, with respect to the dissolved beryllium, at least one impurity from solution.

25 According to still further features in the described preferred embodiments, the reacting is performed in a vessel that is fluidly sealed from an outside (ambient) environment.

30 According to still further features in the described preferred embodiments, the reacting is performed at a pressure exceeding a pressure of 1.5 atmospheres absolute (1.5 ata).

According to still further features in the described preferred embodiments, the reacting is performed at a pressure exceeding a pressure of two atmospheres absolute (2 ata).

5 According to still further features in the described preferred embodiments, the reacting is performed at a pressure exceeding a pressure of three atmospheres absolute (3 ata).

#### BRIEF DESCRIPTION OF THE DRAWINGS

10 The invention is herein described, by way of example only, with reference to the accompanying drawings. With specific reference now to the drawings in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention.

15 In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

In the drawings:

20 Figure 1 is a block diagram of the inventive method for processing a beryllium feed source with fluosilicic acid.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

25 The present invention is a method of treating a beryllium feed material, such as a beryllium-containing ore, by reacting the beryllium feed material with fluosilicic acid.

The principles and operation of the method according to the present invention may be better understood with reference to the drawings and the accompanying description.

30 Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of the components set forth in the following

description or illustrated in the drawing. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

5       Reference is now made to Figure 1, in which a method for the reactive dissolution of beryllium from a beryllium feed source 6 is schematically presented. Beryllium feed source 6 is admixed with fluosilicic acid 8 in reaction stage 10. The beryllium present in beryllium feed source 6 largely dissolves. The reaction mixture is subjected to a solid/liquid separation 20, to produce a residue 14 and a beryllium-rich solution 16.

10       Residue 14 may be processed for further retrieval of beryllium values, or may be discarded. Beryllium solution 16 obtained from bertrandite contains a relatively low beryllium concentration of about 600 mg BeO/liter. However, beryllium solution 16 obtained from beryl typically contains about 2,000 – 10,000 mg BeO/liter.

15       It must be emphasized that the production process of the present invention is appropriate for both batch and continuous modes of operation.

      Typically, beryllium feed source 6 is a commercially-available ore containing beryl ( $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ), bertrandite ( $4\text{BeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ), and/or phenakite ( $\text{Be}_2\text{SiO}_4$ ). Often, such commercially-available ores include additional minerals containing aluminum and iron oxides, calcium and alkali oxides or silicates and quartz. In reaction

20       stage 10, various aluminum, silica, and iron-based minerals from beryllium feed source 6 tend to dissolve.

      Sulfuric acid 12 may be added to reaction stage 10. When beryllium feed source 6 is bertrandite, the addition of sulfuric acid 12 is unnecessary, and the dissolution proceeds essentially to completion at a temperature as low as 55°C - 80°C.

25       When beryllium feed source 6 includes beryl, the addition of sulfuric acid 12 may be beneficial. Preferably, the temperature in the reaction stage is at least 110°C, and more preferably, within the range of 150°C – 170°C.

      When sulfuric acid 12 is added to the beryl (beryllium feed source 6) and fluosilicic acid 8 in reaction stage 10, the dissolution of beryllium values is essentially

30       completed (> 95%) within 6 hours and at moderate temperatures. The preferred temperature range is 100°C - 250°C. Because of the aggressive reaction conditions,

high sulfuric acid concentrations (and/or super-atmospheric pressures), and other costs and concerns pertaining to the operation at the higher end of this range, it is preferable to perform the reaction below a temperature of about 200°C.

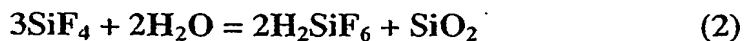
In the reaction of fluosilicic acid with the oxides of beryllium and other cations, the fluosilicates of the various cations are initially produced. Upon heating, silicon tetrafluoride is released, and consequently, little silica remains in the solution, as is evident from the following reaction:



Hence, the reaction temperature is controlled such that the silicon tetrafluoride is evaporated from the reaction mixture in an evaporate 22. The various components of the reaction mixture remain in the solid or liquid phase, such that the evaporation allows for selective removal of the silicon, as silicon tetrafluoride, from the reaction mixture in reaction stage 10.

Of the fluorides thus formed, beryllium fluoride is highly soluble, while the corresponding aluminum salt is sparsely soluble. Because of the common-ion effect, the solubility of aluminum fluorides should be depressed even further. Hence, by concentrating the solution, the concentration of beryllium fluoride increases, and the concentration of the aluminum fluoride decreases.

Evaporate 22, containing exclusively, or substantially exclusively, silicon tetrafluoride and water, is introduced to a silica formation stage 30. Preferably, evaporate 22 is cooled in silica formation stage 30, wherein silicon tetrafluoride and water react to produce a slurry 24 of refined silica and technical-grade fluosilicic acid, according to the following stoichiometry:



Slurry 24 is subsequently filtered in a filtration stage 40. The fluosilicic acid is recycled in stream 32 to reaction stage 10. The filtered silica solids 26 from filtration

stage 40 may undergo further processing (not shown), e.g., drying and/or calcination, to produce high-purity silica.

5 A make-up stream 34 provides a source of fluorine to the process at a rate substantially equal to the process losses of fluosilicic acid along with the production of metal fluorides ( $\text{BeF}_2$ ,  $\text{AlF}_3$ , etc.). Preferably, make-up stream 34 includes fluosilicic acid and/or hydrofluoric acid.

10 The theoretical quantity of fluosilicic acid needed to dissolve the beryllium oxide from the ore must be calculated from the cations of the ore as well as from the silica content. Practically, an excess of fluosilicic acid must be used to achieve the dissolution of the beryllium oxide. However, in addition to the production of amorphous pure silica, the excess fluosilicic acid is recovered.

15 In another preferred embodiment, reaction stage 10 is performed in a closed capsule such as an autoclave or the like, which is hermetically sealed from the environment (i.e., there is no evaporate 22 being discharged from reaction stage 10). Preferably, substantially all of the reaction volume is filled with the reaction mixture. The solution obtained is further processed to recover beryllium values. This method is effective for dissolving various beryllium-containing minerals, and has been found to be particularly effective for directly dissolving raw beryl.

20 After dissolution, the autoclave is opened, and the solution is optionally concentrated by evaporating silicon tetrafluoride and water so as to precipitate aluminum fluoride, which may be removed by filtration.

25 As used herein in the specification and in the claims section that follows, the term "beryllium feed source" refers to a raw material, or combination of raw materials, containing beryllium. "Beryllium feed source" specifically includes, but is not limited to, materials containing beryl, bertrandite, and/or phenakite.

30 As used herein in the specification and in the claims section that follows, the term "directly introduced to the reaction stage" and the like, used in conjunction with "beryllium feed source", refers to a beryllium feed source that is reacted with fluosilicic acid, without first undergoing melting or other high-temperature treatments, and particularly, without undergoing high-temperature treatment at temperatures exceeding 600°C.

As used herein in the specification and in the claims section that follows, the term "source of fluosilicic acid" and the like, refers to fluosilicic acid and/or to any material from which fluosilicic acid is generated in-situ within the reaction mixture. Specifically included within the term "source of fluosilicic acid" are fluosilicates, and more particularly, fluosilicates added to a reaction mixture including an acidic aqueous medium.

The particular operating conditions of the process of the present invention will understandably vary according to the composition of beryllium feed source 6.

#### Advantages of the Inventive Process

- In the known sulfate process for the production of beryllium compounds from beryl, described hereinabove, the multiple-stage thermal treatment is both capital-intensive and energy-intensive (and environmentally hazardous). By sharp contrast, the dissolution of beryllium oxide by means of fluosilicic acid requires no thermal pre-treatment whatsoever.
- The high toxicity of beryllium introduces various safety and ecology issues into the production process. The inhalation of beryllium particles or fumes can trigger acute or chronic lung disease of a serious nature. The inventive process obviates the need for the high-temperature, multiple-stage thermal treatment, significantly reducing thereby the health risk to plant personnel and/or reducing the costs associated with maintaining the requisite high standard of air quality for beryllium production facilities.
- In the conventional heat treatment process, the amount of beryllium dissolved is typically around 90%. In the inventive process, the amount of beryllium dissolved is typically up to 100%, under relatively mild conditions and reasonable residence times.
- In other known processes, a large excess of concentrated sulfuric acid is utilized in the dissolution process, and must be neutralized later in the process. In the present invention, sulfuric acid is hardly necessary, and

certainly not in large quantities. The cost of the sulfuric acid and the neutralizing substance are saved, and the ecological benefits are manifest.

- The leaching of the beryllium oxides from the ores by sulfuric acid occurs at 250-300°C in conventional processes, whereas the inventive process is effective at relatively low temperatures (near 100°C).
- The use of fluosilicic acid in the inventive process enables the production of pure amorphous silica as well as aluminum fluoride as valuable co-product and the recovery of the fluosilicic acid (instead of neutralizing the FSA) to the process. The recovered fluosilicic acid, which is produced from distilled silicon tetrafluoride, is of high purity (technical grade), such that a portion of the recovered fluosilicic acid can be sold, upon demand, to further improve the process economics (while inexpensive fertilizer-grade FSA can be fed to the process in its stead).

Incorporated by reference for all purposes as if fully set forth herein are Israeli Patent Application Serial Nos. IL 140,646, IL 144,038, IL 148,376, and IL 152,802, as well as PCT Application No. PCT/IL01/01210, which draws priority from IL 148,376.

According to a preferred embodiment of the present invention, dissolved impurities in the reaction mixture of reaction stage 10 are selectively precipitated with respect to the dissolved beryllium. By way of example, one major impurity dissolved in the reaction mixture is aluminum ( $\text{Al}^{+3}$ ). At low evaporation (of silicon tetrafluoride) to feed ratios, the  $\text{Al}^{+3}$  is associated with fluosilicate ions ( $\text{SiF}_6^{-2}$ ). At higher evaporation to feed ratios, the  $\text{Al}^{+3}$  precipitates as  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  (or  $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$ ). The beryllium fluoride is highly soluble, such that the beryllium values remain in solution. Hence, the evaporation to feed ratio can be advantageously controlled so as to precipitate various impurities from the beryllium-rich liquor.

Moreover, the extremely low solubility of the various fluoride impurities is depressed even further by the presence of the dissolved beryllium fluoride, according to the well-known common-ion effect, which serves to produce a beryllium solution of even higher purity.



The selective precipitation of most of the various impurities can also be effected by controlling the pH of the reaction mixture. A pH of over 1.5 and preferably over 2 has been found to be advantageous.

The solution produced can then be further processed [e.g., using processes known in the art, as outlined in Ullmann's Encyclopedia of Industrial Chemistry, Vol. 4a, Wiley-VCH Verlag GmbH & Co. (1985)] to produce various refined beryllium products, including, but not limited to, beryllium hydroxide and beryllium metal.

### EXAMPLES

Reference is now made to the following examples, which together with the above description, illustrate the invention in a non-limiting fashion.

#### EXAMPLE 1

Bertrandite of the following composition was used: 0.63% BeO, 11.89% Al<sub>2</sub>O<sub>3</sub>, 3.69% CaO, 1.48% Fe<sub>2</sub>O<sub>3</sub>, 3.97% K<sub>2</sub>O, 1.79% MgO, 2.89% Na<sub>2</sub>O, 66.44% SiO<sub>2</sub>, 2.16% F.

25g of the bertrandite feed material were suspended in 185g of 24.5% fluosilicic acid. The suspension was stirred and heated for 2 hours at 98°C. Subsequently, the suspension was cooled, filtered and washed. The total volume of the filtrate and the washing liquor was 200 ml. The analyzed solution contained 772 mg BeO per liter.

The weight of the wet residue was 33.86g, and after drying, the residue weighed 18.93 g. The residue contained quartz, insoluble fluorides including calcium and magnesium fluoride, and aluminum and ferric fluoride.

BeO in feed material:  $25 \times 0.63 \times 10 = 157.5 \text{ mg BeO}$

BeO recovered:  $772 \times 0.200 = 154.4 \text{ mg BeO}$

% of BeO dissolved:  $154.4 \times 100 / 157.7 = 98.1\%$ .

#### EXAMPLE 2

25g of bertrandite were suspended in 184g of fluosilicic acid (24.5% H<sub>2</sub>SiF<sub>6</sub>). The suspension was stirred and heated for 1 hour at 70°C, cooled, filtered and washed.

The volume of the filtrate and the washing was 200 ml. The weight of the residue after drying was 18.6g. The solution contained 712 mg BeO per liter.

BeO recovered:  $712 \times 0.200 = 142 \text{ mg BeO}$

5 % BeO dissolved:  $142 \times 100/157.5 = 90.3\%$

### EXAMPLE 3

15g of bertrandite were suspended in 109g of fluosilicic acid (24.5%  $\text{H}_2\text{SiF}_6$ ). The suspension was stirred and heated for 0.5 hour at  $72^\circ\text{C}$ . After cooling, filtering,  
10 and washing, 140 ml of solution were obtained. The solution contained 599.8 mg of BeO per liter.

BeO in feed material:  $15 \times 0.63 \times 10 = 94.5 \text{ mg}$

BeO recovered:  $599.8 \times 0.140 = 84.0 \text{ mg}$

% BeO dissolved:  $84.0 \times 100/94.5 = 88.9\%$

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### EXAMPLE 4

25g of bertrandite and 180ml of fluosilicic acid (29.26%  $\text{H}_2\text{SiF}_6$ ) were stirred and heated for 2.0 hours at  $73^\circ\text{C}$ . After cooling, filtering, and washing, 205g ml of solution were obtained. The solution contained a total of 732.2mg of BeO per liter. The  
20 dissolved beryllium represented 95.3% of the beryllium in the feed material.

### EXAMPLES 5-7

Samples of bertrandite were reacted with fluosilicic acid (24% - 29%  $\text{H}_2\text{SiF}_6$ ) for 1-2 hours at temperatures between  $70^\circ\text{C}$  and  $90^\circ\text{C}$ . The results are summarized below  
25 in Table 1:

TABLE 1

	T ( $^\circ\text{C}$ )	Duration (h)	% Excess FSA <sup>1</sup>	Be Yield (%)
EXAMPLE 5	87	1	110	91.8
EXAMPLE 6	71	1	108	82.5
EXAMPLE 7	70	2	20	92.0

<sup>1</sup>% Excess fluosilicic acid (FSA) calculated on all ore components other than silica

EXAMPLE 8

To 10g of finely ground beryl containing 13.08% BeO, 17.25% Al<sub>2</sub>O<sub>3</sub>, 0.91% Fe<sub>2</sub>O<sub>3</sub>, 63.91% SiO<sub>2</sub>, 0.19% MgO, 0.7% Na<sub>2</sub>O, 1.4% ZrO, and 0.35% PbO, were added 100g of concentrated sulfuric acid (98% H<sub>2</sub>SO<sub>4</sub>). Slowly, in drops, 403g of fluosilicic acid (29.3% H<sub>2</sub>SiF<sub>6</sub>) were introduced. The temperature rose to 150°C, and the mixture was allowed to react for 6 hours. The product of the condensed vapors was found to contain pure amorphous silica and fluosilicic acid. After filtration of the silica, the FSA was conserved for the next batch. The suspension produced was cooled and filtered, and the residue was washed to retrieve beryllium values. The dried residue weighed 2.03g.

The volume of the filtrate and washing liquor was 200ml. The beryllium content of the liquor, expressed as beryllium oxide, was 6,180mg BeO/liter solution. The percent dissolution of beryllium was calculated to be  $6,180/1,308 \times 0.200 \times 100 = 94.5\%$ .

The aluminum concentration of the combined filtrate and washing liquor was 10,465mg Al<sub>2</sub>O<sub>3</sub>. The percent dissolution of the aluminum was  $10.465 \times 0.2 \times 100/15/0.1725 = 80.9\%$ . The iron content of the solution was 605mgFe<sub>2</sub>O<sub>3</sub>/liter. The percent dissolution of the iron was  $0.605 \times 0.2 \times 100/15/0.0091 = 88.6\%$ .

EXAMPLE 9

To 10g of finely ground beryl containing 13.08% BeO, 17.25% Al<sub>2</sub>O<sub>3</sub>, and 0.91% Fe<sub>2</sub>O<sub>3</sub>, were added 500g of fluosilicic acid (29.3% H<sub>2</sub>SiF<sub>6</sub>), and 9.2g of sulfuric acid (98% H<sub>2</sub>SO<sub>4</sub>). The mixture was evaporated to dryness in a graphite reactor, and cooled. 150ml of 0.1 N HCL were then added, the reactor being stirred by a magnetic stirrer. After 0.5 hours of stirring at room temperature, the mixture was filtered. The residue, after washing and drying, weighed 5.56g. The total volume of the filtrate and washing liquor was 170ml. The solution contained 6892 mg/l BeO, 893 mg/l Al<sub>2</sub>O<sub>3</sub> and 153 mg/l Fe<sub>2</sub>O<sub>3</sub>.

% dissolution of BeO was:  $6.892 \times 0.170 \times 100/1.308 = 89.6\%$

% dissolution of Al<sub>2</sub>O<sub>3</sub> was:  $0.893 \times 0.170 \times 100/1.725 = 8.8\%$

% dissolution of Fe<sub>2</sub>O<sub>3</sub> was:  $0.153 \times 0.170 \times 100/0.091 = 28.6\%$

The concentration of impurities (Al, Fe) relative to that of Be in the final solution was much lower than in the final solution of Example 8.

### EXAMPLE 10

As in Example 9, a total of 150ml of 0.1N H<sub>2</sub>SO<sub>4</sub> was used for leaching. The dried residue weight was 3.34g. The volume of the filtrate and washing was 175g. The solution contained 5.75mg BeO per 1g solution, 1202 ppm Al<sub>2</sub>O<sub>3</sub>, and 55ppm Fe<sub>2</sub>O<sub>3</sub>.

% dissolution of BeO was:  $5.72 \times 175 \times 100 / 1000 / 1.308 = 76.5\%$

% dissolution of Al<sub>2</sub>O<sub>3</sub> was:  $1202 \times 175 \times 100 / 1,000,000 / 1.725 = 12.2\%$

% dissolution of Fe<sub>2</sub>O<sub>3</sub> was:  $55.175 \times 100 / 1,000,000 / 0.091 = 10.6\%$

The concentration of impurities (Al, Fe) relative to that of Be in the final solution was much lower than in the final solution of Example 8.

### EXAMPLES 11-15: Dissolution of beryl in a sealed capsule

To a Teflon® (polytetrafluoroethylene)-lined capsule having a reaction volume of 60 ml were added 1 gram of beryl and 58-60ml of fluosilicic acid (29.3% H<sub>2</sub>SiF<sub>6</sub>), such that substantially the entire volume of the capsule was filled with the reaction mixture. The capsule was hermetically sealed and placed in an oven that was heated up to a specified temperature. After pre-determined times, the capsule was cooled and opened.

The content of the capsule was filtered, the solid residue was washed, dried and weighed. The results are summarized in Table 2 below:

**TABLE 2**

Example No.	Beryl quantity (grams)	Acid quantity (ml)	Excess <sup>1</sup> (%)	Temperature (°C)	Experiment Duration (hours)	Residue (grams)	Dissolution of solids (%)
11	1	60	358	125	10	0.15	85
12	1	60	358	125	16	0.02	98
13	1	60	358	140	6	0.15	85
14	1	60	358	140	12	0.07	93
15	1	60	358	160	3	0.02	98

<sup>1</sup>% Excess fluosilicic acid (FSA) calculated on all ore components other than silica

EXAMPLES 16-17: Dissolution of beryl in a sealed capsule

To a pre-heated Teflon®-lined capsule having a reaction volume of 120 ml, were added finely ground beryl (containing 12.25% BeO, 17.5% Al<sub>2</sub>O<sub>3</sub>, and 1.0% Fe<sub>2</sub>O<sub>3</sub>) and 100ml of fluosilicic acid (29.3% H<sub>2</sub>SiF<sub>6</sub>), along with a Teflon®-coated iron stirring rod.

5 The capsule was hermetically sealed and placed in a thermal-oil bath resting on a magnetic-stirring heating plate. The capsule was stirred and maintained at 160°C (well above atmospheric pressure) for a pre-determined time. After cooling, the capsule was opened, and the content of the capsule was filtered, and the solid residue was washed, dried and weighed. The results are summarized in Table 3 below:

10

TABLE 3

Example No.	Beryl quantity (grams)	Excess <sup>1</sup> (%)	Experiment Duration (hours)	Dry Solids incl. precipitate (grams)	Dissolution of Be (%)
16	1.67	358	2.5	0.02	100
17	5.0	53	3	2.31	96.6

<sup>1</sup>% Excess fluosilicic acid (FSA) calculated on all ore components other than silica

Although the invention has been described in conjunction with specific

15 embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims. All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the

20 specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

## WHAT IS CLAIMED IS:

1. A production process for dissolving beryllium in a beryllium feed source by means of fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ), the process comprising the steps of:
  - (a) providing the beryllium feed source, and
  - (b) reacting the beryllium feed source with a source of fluosilicic acid in a reaction stage to produce dissolved beryllium in an aqueous solution.
2. The process of claim 1, wherein the beryllium feed source contains a source of silica, the method further comprising the step of:
  - (c) subjecting said source of silica and the fluosilicic acid to a reaction, so as to produce silicon tetrafluoride and water.
3. The process of claim 2, further comprising the step of:
  - (d) selectively evaporating said silicon tetrafluoride with respect to said dissolved beryllium.
4. The process of claim 1, wherein said reaction stage contains a solid residue along with said aqueous solution, the method further comprising the step of:
  - (c) separating said aqueous solution from said solid residue.
5. The process of claim 1, wherein said reacting is performed at a temperature above  $60^\circ\text{C}$ .
6. The process of claim 1, wherein said aqueous solution includes beryllium fluosilicate.
7. The process of claim 1, wherein said aqueous solution includes beryllium fluoride.

8. The process of claim 1, wherein said aqueous medium contains the fluosilicic acid and at least a second acid, said second acid having a concentration of less than 10% by weight.
9. The process of claim 8, wherein said second acid has a concentration of less than 5% by weight.
10. The process of claim 8, wherein said second acid has a concentration of less than 2% by weight.
11. The process of claim 8, wherein said second acid is selected from the group consisting of sulfuric acid, hydrochloric acid, hydrofluoric acid, and phosphoric acid.
12. The process of claim 9, wherein said second acid is sulfuric acid.
13. The process of claim 1, wherein said beryllium feed source includes beryl.
14. The process of claim 13, wherein said beryllium feed source is directly introduced to said reaction stage.
15. The process of claim 13, wherein said reacting is performed at a pressure exceeding atmospheric pressure.
16. The process of claim 3, further comprising the step of:
  - (e) reacting said silicon tetrafluoride with water to produce silica and regenerated fluosilicic acid.
17. The process of claim 16, further comprising the step of:

- (f) recycling at least a portion of said regenerated fluosilicic acid to said reaction stage.

18. The process of claim 16, wherein said reacting of said silicon tetrafluoride with said water includes cooling to a temperature below 75°C.

19. The process of claim 16, wherein an excess of the fluosilicic acid is introduced to the process, such that at least a portion of said regenerated fluosilicic acid is removed as a co-product.

20. The process of claim 1, wherein said beryllium feed source includes a beryllium-containing material selected from the group consisting of bertrandite and phenakite, and wherein said aqueous medium contains less than 10 weight % of sulfuric acid.

21. The process of claim 20, wherein said aqueous medium contains less than 5 weight % of sulfuric acid.

22. The process of claim 1, wherein said beryllium feed source includes a beryllium-containing material selected from the group consisting of bertrandite and phenakite.

23. The process of claim 22, wherein said reacting is performed at a temperature below 200°C.

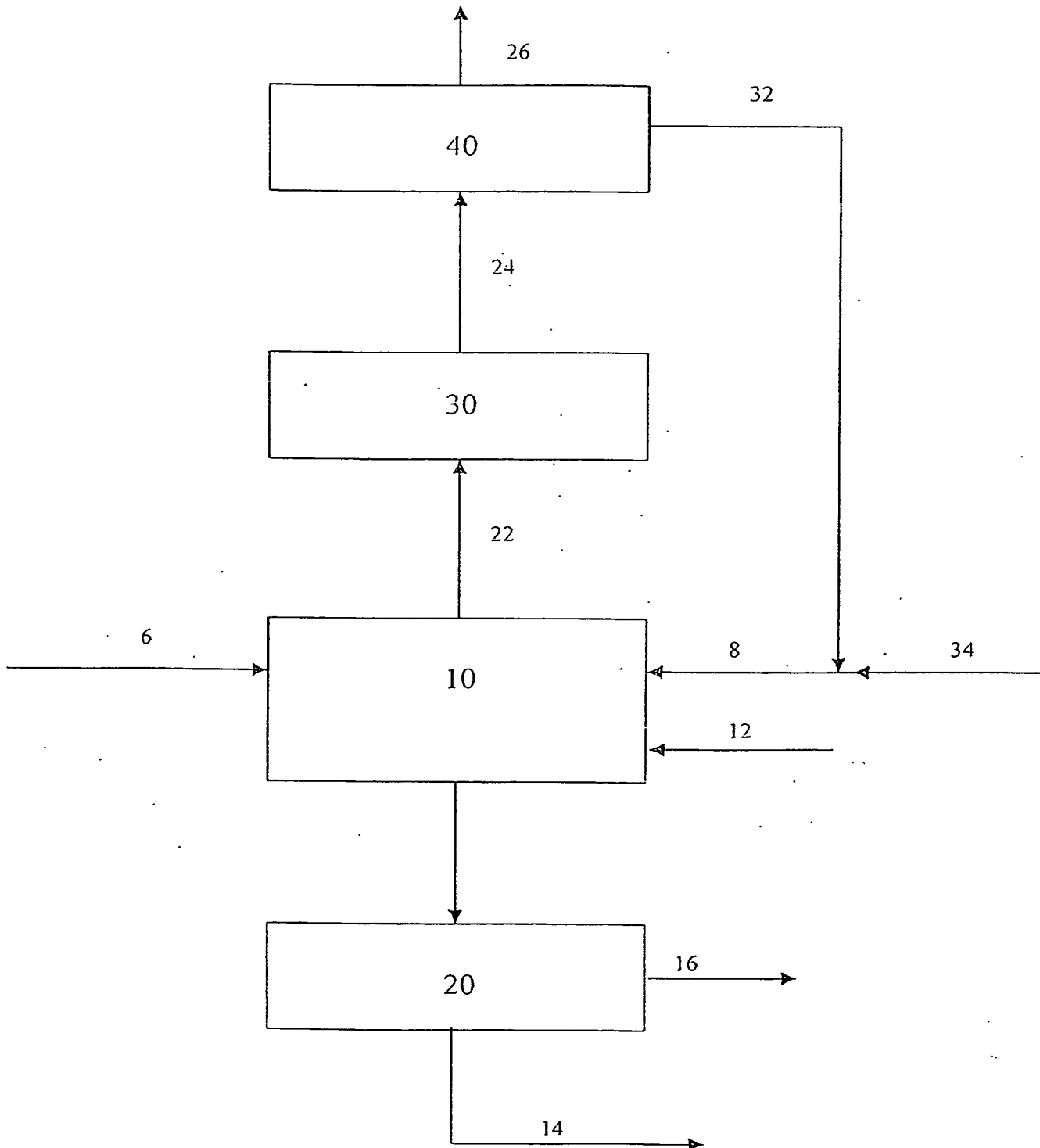
24. The process of claim 22, wherein said reacting is performed at a temperature below 150°C.

25. The process of claim 3, wherein evaporation of said silicon tetrafluoride is controlled so as to selectively precipitate, with respect to said dissolved beryllium, at least one impurity from solution.



26. The process of claim 25, wherein said at least one impurity is a fluoride.
27. The process of claim 25, wherein said at least one impurity includes a cation selected from the group consisting of aluminum and iron cations.
28. The process of claim 3, wherein a pH of said aqueous solution is controlled so as to selectively precipitate, with respect to said dissolved beryllium, at least one impurity from solution.
29. The process of claim 1, wherein said reacting is performed in a vessel that is fluidly sealed from an outside environment.
30. The process according to claim 1, wherein said reacting is performed at a pressure exceeding a pressure of 1.5 atmospheres absolute (1.5 ata).
31. The process according to claim 1, wherein said reacting is performed at a pressure exceeding a pressure of two atmospheres absolute (2 ata).
32. The process according to claim 1, wherein said reacting is performed at a pressure exceeding a pressure of three atmospheres absolute (3 ata).
33. The process according to claim 1, wherein said source of fluosilicic acid includes fluosilicic acid.
34. The process of claim 9, wherein said second acid is hydrofluoric acid.

FIGURE 1



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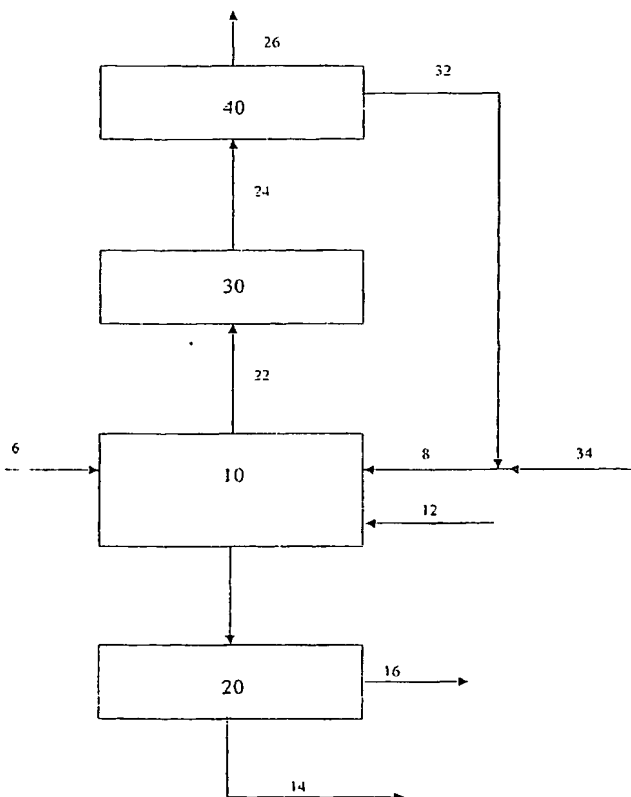
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(54) Title: METHOD OF LEACHING BERYLLIUM FROM BERYLLIUM-CONTAINING ORES USING FLUOSILICIC ACID



(57) Abstract: A production process for dissolving beryllium in a beryllium feed source by means of fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ), including the steps of: (a) providing the beryllium feed source, and (b) reacting the beryllium feed source with a source of fluosilicic acid in a reaction stage to produce dissolved beryllium in an aqueous solution.

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 1,960,986 (BEJA et al) 29 May 1934 (29.05.1934), Whole Article	1-7, 11, 13,
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Y		16, 18, 25-27
Y	US 3,375,060 (OLSON et al) 26 March 1968 (26.03.1968), Column 1, Line- 71 to Column 2, Line- 11; Line-62	11-15, 20-27
A	US 3,699,208 (GRUNIG et al) 17 October 1972 (17.10.1972), whole article	1-34
A	US 3,411,868 (MORANA et al) 19 November 1968 (19.11.1968), whole article.	1-34
Y	JP 58-176120 A (AGENCY OF IND SCIENCE & TECHNOL) 15 October 1983 (15.10.1983), Abstract.	11-12, 34
Y	GB 1,252,081 (ANACONDA CDOMPANY) 03 November 1971 (03.11.1971), Page-1, Lines: 53-98)	11-14, 25-28

☐ Further documents are listed in the continuation of Box C.

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